MOISTURE-SOLID RELATIONSHIPS ACCOMPANYING DRYING OF LEATHER

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Abstract

By utilizing mathematical principles of surface chemistry and knowledge about the structure of collagen and hides, it is possible to follow the events which occur during different stages of water removal from leather.

When water is removed from the space between fibrils, lateral shrinkage of fibers occurs. High-rate, longitudinal shrinkage of fibers takes place when the ends of successive molecules in the same row approach each other. Whereas this is observed to occur where the average moisture content drops from about 50% (moisture-free basis) to about 27%, mathematical evidence is presented which indicates that longitudinal shrinkage diminishes actually at about 9% moisture content when end-to-end contact between molecules is prevented due to accumulation of chrome in the region of d-bands of positively stained fibrils of collagen seen by electron microscopy. This may be one of the mechanisms through which tanning prevents bonding of molecules together and preserves elasticity and flexibility in leather. Calculations show that chemical or physical reaction between different parts of the hide structure should be small if the moisture content in every part of the hide or leather is kept above roughly 13%. Using published information, mathematical equations are derived describing shrinking and stressing of leather during drying.

Introduction

In recent years the techniques used by the industry for drying of leather are changing as vacuum drying, automated toggling, high frequency drying, and microwave drying are being introduced to replace the older air drying operations and to help tanners compete on the basis of superior leather quality. These changes demand not only a thorough understanding of the general drying principles, but also an intimate knowledge of the events which occur inside the leather structure during drying if optimum conditions from the standpoint of leather quality and yield are to be selected by a tannery in the manufacture of different products. Whereas the theory applicable to the drying of leather has been thoroughly reviewed by Buck[1], by Krischer[2] and others, that theory is inadequate to fully explain many important phenomena encountered in actual practice. Surface chemistry and knowledge about collagen structure are applied in this paper to published data on drying of leather to explain where and what changes occur in the hide structure during different stages of drying, how they induce volume shrinkage and tensile stresses, and (partially) why tanning transforms hides into leather.

EFFECT OF CAPILLARY FORCES ON THE HIDE STRUCTURE

The primary building block of hide is the collagen molecule which is 300 nm long, and 1.5 nm in diameter[3]. These molecules are aggregated into fibrils with an average diameter of 155 nm when cattle are about 40 months old[4]. Clusters of fibrils yield fibers 2800 nm

in diameter. Finally, a collection of fibers forms fiber bundles. Spaces between each of these fibrous constituents are filled with water and non-collagenous constituents such as proteoglycans. Additional water enters these spaces when the non-collagenous materials are removed during pre-tanning. The diameter of the water-filled pores is about 1.6 nm between molecules. The distance between fibrils varies with age of the animal. At 40 months it is roughly equal to 155 nm, the average diameter of a fibril.

The collagen molecules in the fibril are stacked end-to-end (or head to tail) with a gap of 36 nm between them, and side-to-side in a quarter-staggered array approximately 1.5 nm apart[5]. The partial overlapping permits formation of covalent crosslinks close to each end of the molecule (at the points of overlapping) which stabilizes and reinforces the structure. For every five molecules in the overlap zone, only four occur in the adjacent gap zone. Because of that, the overlap and gap zones are visible by electron microscopy and X-ray diffraction as regular transverse bands, the so-called D-periods, with an axial periodicity of 60-70 nm. In hydrated rat-tail tendon, which has been studied most thoroughly, the D-period is equal to 67 nm and its gap zone is about 36.2 nm long.

When moisture is removed from collagen fibrils, no change in the side-to-side distance, d_m, occurs until a critical moisture content is reached[6], which varies with type of collagen tissue, being about 120% in kangaroo-tail tendon, 110% in hides from young cattle and lower (about 70%) in hides from old cattle. As will be shown below, this critical moisture content corresponds to the point during dehydration at which the length of the gap zone begins to decrease, or even somewhat earlier when water from the interfibrillary space is being removed. It is a consequence of a drop in hydrostatic pressure[7] induced in small capillaries by capillary attraction.

The surface of a tissue rich in collagen, such as a hide, has both large and small capillaries. During the initial stages of drying the water lost from smaller capillaries is quickly replaced by water transferred by capillary "suction" from the large pores. The structure shrinks somewhat because the film of water between the large particles, the fiber bundles and the fibers, tends to diminish in an attempt to decrease its surface area between the particles. This surface-area reduction is limited, however, because the particles are rigid and oriented in all directions while the capillary attraction is small in large pores.

After the larger pores have lost their water, the smaller, interfibrillar capillaries begin to lose theirs and a second, low-rate shrinkage stage begins. These changes can be mathematically described by the following calculations[7]. At 20°C, the hydrostatic pressure, P_{12}, in the 155 nm interfibrillar capillaries is equal to

$$P_{12} = -\frac{2\tau}{r} \qquad (1a)$$

$$= \frac{-2\,(72.8 \times 10^{-3})}{77.5 \times 10^{-9}}$$

$$= -1.88 \times 10^{6}\ \mathrm{N/m^2} = -18.2\ \mathrm{atm}$$

where

P_{12} = hydrostatic pressure
τ = surface tension of water, N/m
r = radius of capillary, m

This is greater than the 3.5 atm osmotic swelling pressure[8] which concentrated solutions of glycosaminoglycans, present in the interfibrillary space, are capable of generating to

oppose the above drop in hydrostatic pressure. Because the interfibrillary capillaries are practically all of the same size, because of their large number, and because the osmotic pressure is insufficient to oppose the effects of the hydrostatic pressure drop, a noticeable degree of shrinkage is to be expected.

A further increase in the rate of shrinkage occurs when the water is being removed from the 36.2 nm gap zone. Using equation (1a) it is seen that the drop in hydrostatic pressure would be -78 atm. The high reduction in hydrostatic pressure causes a proportionate reduction in vapor pressure of water from P_s to P described by the equation[9]

$$ln \frac{P}{P_s} = \frac{V_1 (P_{12} + P_{11})}{RT} \quad (1b)$$

With this equation,

$$ln \frac{P}{P_s} = \frac{(18.04)(-78 - 1)}{(82.05)(293)} = -0.0593$$

$$\frac{P}{P_s} = 0.94 \text{ (i.e., 94\% relative humidity)}$$

where

V_1 = molar volume of water, cm^3/mole
P_{11} = atmospheric pressure = 1 atm
R = gas constant, cm^3 atm/°K mole
T = temperature, °K

According to the equilibrium moisture isotherm for rat-tail tendon, this percent relative humidity in the air is in equilibrium with about 80% moisture content in the tendon. This is close to the reported critical moisture content referred to above and identical to the hygroscopic point mentioned below when discussing drying. Similar calculations show that the 155 nm capillaries between the fibrils are emptied at 99% relative humidity when the moisture content is over 100%.

Rougvie and Bear[10] determined by X-ray diffraction that both d_m and D (the side-to-side distance between molecules and the D-period, respectively) decrease with removal of moisture and that a plot of d_m vs D yields a straight line down to 9% moisture content. To understand the reason for these changes, it is helpful to consider that the drop in hydrostatic pressure occurs in the capillaries just below the meniscus near the surface of the sample of tissue rich in collagen. As water evaporates from the small intermolecular capillaries, it is replaced by water from the interfibrillary spaces which get reduced in size in the process. Once the interfibrillary spaces are decreased to the size of the gap zone, water from the gap zones is pulled into the intermolecular capillaries. To fill the void created in the gap zones, the telopeptides on the ends of molecules are pulled in and, finally, there is some movement of the molecules themselves into the void space in the gap zone made possible by alignment of the amino acid side chains forming the covalent crosslinks from a position perpendicular to the axes of the molecules to a position diagonal or almost parallel to them. Examination of band patterns of positively stained fibrils by electron microscopy reveals that the N-ends of molecules (located at the left-hand margin of each

stain-excluding overlap zone) lie in the vicinity of the c_2 bands in the fibril, while the C-ends are in the vicinity of the a_3 bands[11]. Using X-ray diffraction Chandross and Bear[12] showed that after dehydration to 18% moisture content, the ends of the N and C telopeptides cover most of the e and all of the c bands as the gap zone gets reduced by as much as 22.2 nm, from 36.2 nm to 14 nm, while the D-period drops in length only by 3 nm, from 67 to 64 nm.

When the moisture has dropped to 9%, and d_m is equal to 1.06 nm while D = 63.7 nm, a big change occurs in the rate of decrease in the length of D with water content[10]. Up to that point the decrease in the length of the gap zone occurred because water was being removed from it by the pull of the smaller intermolecular capillaries. Calculations using equations (1a) and (1b) along with the equilibrium moisture isotherm for kangaroo-tail tendon indicate that the interparticle distance should be 1 nm at 9% moisture content, whereas experimental determination shows it to be 14 nm in the gap zone. This apparent anomaly is readily explained by considering (i) that Namura *et al*[13] found only structural water to be present at 0-7% moisture content whereas water in a 14 nm space would be bound water and (ii) that according to the literature[14] glycosaminoglycans and glycoproteins are present in the gap zones in the neighborhood of d/e staining bands. It is reasonable to conclude, therefore, that at 9% moisture content, when the gap zone is slightly below 14 nm in length, the ends of the telopeptides have approached the glycosaminoglycan rich area of the gap zone to within 1 nm and that now the interparticle spaces in gaps are of the same order of magnitude as the intermolecular spaces. With further loss in moisture from the gap zones, the molecules experience further compression but their ends stop stretching. Support for his viewpoint is found in the fact that the 50 nm length of the overlap zone observable at 18% moisture does not increase further even when very high temperatures are used to remove all of the structural water[15].

Thus, experimental X-ray diffraction data gives a mathematical relationship between d_m and D:

$$d_m = a\,D + b \tag{2a}$$

Using experimental data[10] a = 0.09 and b = -4.66.

From electron microscopy, one obtains

$$D = d_o + d_g \tag{2b}$$

where

d_o = length of the overlap zone

and d_g = length of the gap zone

Considering that the gap zone contains an approximately 13 nm long space rich in glycosaminoglycans

$$d_g = 13 + 2d \tag{2c}$$

where d is the interparticle space in the gap filled with water subject to capillary attraction. For any given moisture content, the d value can be calculated from equations (1a) and (1b) with the help of the equilibrium moisture isotherm. If, in addition, either d_m or D is known, equations (2a) to (2c) yield all the other dimensions.

DRYING RATES

The capillaries in the hide can be divided into four distinct groups, largest to smallest, as follows: among fibers and fiber bundles, between fibrils, between the ends of molecules in the same row, and in the side-to-side space between molecules. Consequently, drying of leather would involve four stages if it were accomplished at an infinitely slow rate, assuring complete moisture equilibrium between all the constituent parts.

In the first drying stage, the so-called constant-drying-rate period, the surface would remain wet and the water would evaporate into the surrounding air at a constant rate. The water level in the large capillaries would recede into the leather while the water lost from the small capillaries would be quickly replaced by the water transferred by capillary suction from the larger capillaries. The temperature at the surface would be at the wet bulb temperature of the air. The rate of evaporation of the unbound water, dW/dt, would be proportional to the difference between the vapor pressure of the water at the surface temperature, P_s, and the partial pressure of the water vapor in the air, P_a

$$\frac{dW}{dt} = KgA(P_s - P_a)$$

where K_g = mass transfer coefficient
and A = area of heat and mass transfer

At about 70% moisture content, i.e. at the hygroscopic point, the larger pores would be almost empty and drying would enter the first falling-rate period. The remaining water would be bound water present in the capillary spaces among fibers, and molecules. At this time, the vapor pressure of the water in the smaller capillaries would be lower (with large capillaries $P \approx P_s$) and the drying rate would be slower and would constantly decrease. With time, the surface at which drying is taking place would slowly start to recede into the inner layers of the hide and the reduction in capillary diameter would cause fibrils to come closer together, decreasing P even further. The drying rate would thus slowly decrease due to the constantly decreasing vapor pressure and the increasing distance between the drying surface and the outer surface of the leather which would decrease the value of the mass transfer coefficient, K_g. A second falling rate period might then be observed at $P/P_s = 0.95$ (i.e. at 95% R.H.) when most of the interfibrillar water had left the leather and the water from the gaps between the ends of molecules would be removed. Finally, if drying were to continue, a third falling-rate period would be detected at 9% moisture content when all bound water had left the sample.

A review of the literature[1,2,16,17] reveals that the results are somewhat different when leather is dried under practical drying conditions. A constant drying period may or may not be observed depending on the initial moisture content of the leather. As drying proceeds, a condition is soon reached at which the surface is at 50-70% moisture content (the hygroscopic moisture content, X_{hyg}) and the center of the hide is at the original moisture content. The average moisture content would depend on leather thickness, initial moisture content and drying conditions[16]. In the absence of unbound moisture at the surface, a change in drying rate is observed at this average moisture content, often called the critical point, X_c. The constant-drying rate ceases at this critical point and the drying operation enters the first falling-rate period. In this drying period the moisture at the center decreases and approaches the moisture content, X_{hyg}, corresponding to the hygroscopic point while the surface is already at the moisture content X_{eg}, which is in equilibrium

with the surrounding air. The second falling-rate period then commences when the average moisture content has reached a value equal to $(X_{hyg} + X_{eg})/2$. Drying ceases when the moisture content has reached the equilibrium value, X_{eg}, in all parts of the leather. Thus, under practical drying conditions the moisture content, at any time, varies over a wide range depending on the location in the leather.

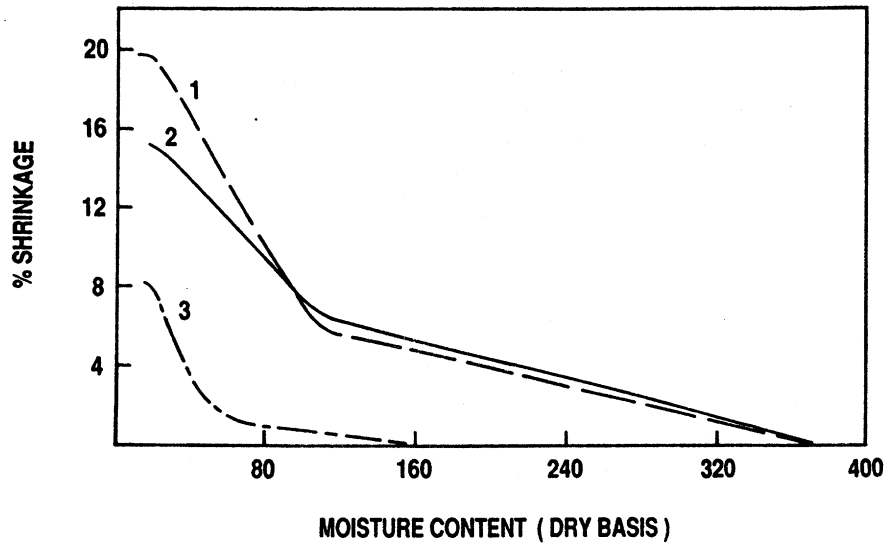

FIG. 1 — Percent shrinkage at different moisture contents (on dry basis) during drying of unrestrained strips of chrome leather. Calf Leather (data excerpted from Freudenberg[17]):
Line 1—Dry-bulb temperature 60°C, relative humidity 20%, strip size 100 mm x 10 mm. Line 2—Dry-bulb temperature 60°C, relative humidity 60%, strip size 100 mm x 10 mm.
Cowhide Leather (data excerpted from Spiers and Pierson[18]): Line 3—Dry-bulb temperature 37.8°C, relative humidity 41%, strip size 254 mm x 25.4 mm.

SHRINKING OF LEATHER DURING DRYING

Plots of percent linear shrinkage vs. moisture content (moisture free basis) are shown in Figure 1. This information was constructed from experimental data obtained from the literature on longitudinal shrinkage of strips of chrome leathers during drying. The data which were obtained by Freudenberg[17] and Spiers and Pearson[18] were selected to demonstrate the great differences in published results. Freudenberg reported much higher shrinkage values (lines 1 and 2) because he dried calf leather, while Spiers and Pearson (line 3) dried cowhide leather. Lines 1 and 2 show the difference in shrinkage obtained at different drying conditions. Drier air induces more shrinkage as shwon by comparing lines 1 and 2, which represent dehydration at 20% R.H., and 60% R.H. respectively. The same dry-bulb temperature (60°C) was used in both cases. Each of the plots in Figure 1 shows 3 shrinkage stages. In all cases, the shrinkage that ends at about 27% moisture content contributes most of the shrinkage. This high-rate shrinkage stage starts at about 110% moisture content, for calf leather and at about 48% moisture content for cowhide leather. As will be explained below, it starts much sooner for the former because the fibrils and fibers in calfskins are much smaller in diameter[4] and because there is much more water in the spaces between them.

Based on the definition of shrinkage[20] and the linear shrinkage coefficient, δ

$$\text{Shrinkage} = \frac{LI - Lt}{LI}$$

$$= \frac{LO(1 + \delta XI) - LO(1 + \delta Xt)}{LI}$$

$$= \frac{LO\,\delta(XI - Xt)}{LI} \qquad (3)$$

where Lt and Xt = Length of leather sample and its moisture content, respectively, at the time t;

LI = initial length;

LO = length of the sample at zero percent moisture content; and

XI = initial moisture content;

δ = (wet length/dry length)/(weight of water/weight of dry hide solids)

Application of equation (3) to the data shown in Figure 1 yields the same value of approximately 0.075 for the overall, linear shrinkage coefficient, δ, in the longitudinal direction (parallel to the surface) for both calf and cowhide leather. Experimental data (not shown) published by Spiers and Pearson[18] on toggled discs of chrome tanned cowhide leather yield values of about 0.22 for the coefficient of shrinkage in thickness. Both of these values are in close agreement with values reported by Luikov[19]. However, the data by Spiers and Pearson give a value of approximately 0.079 for δ for shrinkage in thickness of unrestrained discs of chrome leather. Thus, for unrestrained chrome leather the coefficient of linear shrinkage is numerically almost equal in all directions, and it may be possible to calculate shrinkage in volume of unrestrained leather replacing L with V and δ with ß = 3δ[20]. Of course, leather is anisotropic and it may be preferable if more exact results are desired to use separate δ values for shrinkage along axes in different directions.

Even in the same direction, leather shrinks in four stages with zero or practically no shrinkage in the first stage, low-rate shrinkage in the second, high-rate shrinkage in the third, and low-rate shrinkage in the fourth (and last) stage.

Consequently, for leather

Total shrinkage =

$$\frac{LO[\delta 1(XI - X1) + \delta 2(X1 - X2) + \delta 3(X2 - X3) + \delta 4(X3 - X4)]}{LI} \qquad (4)$$

Where δ1, δ2, δ3, and δ4 are the linear shrinkage coefficients for stages 1 to 4 in units of length per unit length per moisture content (dry basis), and X1, X2, X3 are the moisture contents at the end of shrinkage stages 1, 2, and 3, respectively. As can be determined from Figure 1, δ1 = 0, δ2 = 0.013, δ3 = 0.2, X1 = 1.8, X2 = 0.48, and X3 = 0.27 g/g for chrome leather from cowhide. Because the capillaries between fibrils are larger in calfskins, the initial moisture content, XI, is higher (3.7 g/g) and X2 = 1.1, while δ2 = 0.024 and δ3 = 0.26.

Different leathers are often compared in terms of porosity, apparent density, volume gain and similar properties which are closely related to the degree of shrinkage attained during drying. Various tannages yield leathers which give different values for these pro-

perties. Stather and Reich[21] found that 0.65-0.75 cm^3 of dry chrome leather is obtainable from 1 cm^3 unhaired and bated cattlehide. Assuming the volume of chrome-tanned hide to be approximately equal to the volume of limed hide, it is easily shown that

$$\text{Volume shrinkage} = \frac{(V_{wet} - V_{dry})}{V_{wet}}$$

$$= \frac{(1 - 0.70)}{1} = 0.30 \text{ or } 30\%$$

Spiers and Pearson[18] and many others report the same results for percent volume shrinkage of chrome-cowhide leather. However, for leather from similar hides, the percent shrinkage is also a function of the type and degree of tannage.

TABLE I

Distance Between Particles at Different Moisture Contents

Distance Between Particles d nm	Moisture (Dry Basis) %	Relative Humidity At Equilibrium %	Temperature °C	Comments
>155	--	--	--	Practically no shrinkage
155***	70+ (Estimate)	99	40	Low-rate shrinkage starts
40**	50 (Estimate)	95	40	High-rate shrinkage begins
19*	35	90	40	High-rate shrinkage continues, staking easy
2*	13	39	40	Side chains of molecules start interacting
1*	8	15	40	Sides of molecules touch, overlap zone stops increasing
8.2*	27	78	27	High-rate shrinkage ends
8.6*	27	80	38	High-rate shrinkage ends
10.6*	27	85	60	High-rate shrinkage ends
10*	30	81	20	Staking is possible
10.2*	30	83	32	Staking is better

***Distance among fibrils.
**Distance between ends of successive molecules in gap zone.
*Distance between fibrils and molecules. Distance of gap zone greater by 13 nm.

Discussion

A thorough review of the literature on drying of leather sheds little light on the mechanism that is responsible for shrinkage or creation of tensile forces. Only by considering capillary attraction in conjunction with the structural arrangement of the fibrous particles in the hide does a clearer picture of the actual events emerge. Following a first

shrinkage stage involving practically no shrinkage at all, shrinkage of chrome leather from cowhide undergoes a rate change at almost exactly the hygroscopic point. Fibers and fiber bundles in the grain layer of cowhide are to a very large extent parallel to the hide surface, but they extend in different directions. The void spaces between them are relatively large and the capillary forces are too small to overcome their natural stiffness, which is reinforced by the stiffening effect introduced by tanning. Consequently, during the first (preliminary) shrinkage stage (which roughly corresponds to the constant rate drying stage in which free or unbound moisture is removed) the voids are emptied with little or no shrinkage of the leather structure.

Unlike fibers, the fibrils are stacked parallel to each other. Consequently, they approach each other more readily when moisture is being removed from the space between them, especially since this distance is small enough (155 nm in cowhide, see Table 1) for significant capillary attraction. The shrinkage rate thus enters the second phase as soon as water begins to leave the space between the fibrils. Since hide consists of a random network of collagen fibers interconnected by thinner aggregates of fibrils branching out from one fiber to another, it is difficult to calculate the percent shrinkage that occurs during this stage. As shown in Figure 1, while chrome leather from calfskins shrinks about 6% during this stage, chrome leather from cowhides shrinks only 1.5%, simply because calfskins have thinner fibrils with more space (and water) between them. With chrome calf leather this stage ends at about 110% moisture content and with chrome-cowhide leather at about 48% moisture content.

Fibers undergo both lateral and longitudinal shrinkage. This occurs during the third shrinkage stage when the fibrils have approached within 36 nm of each other, which is equal to the length of the gap between successive collagen molecules in a row. Calculations by the author show that the capillary attraction between two molecules in this gap is more than sufficient to stretch the molecules and to keep on stretching them as the gap between them is being diminished. The parts of the molecule which undergo most of the stretching are the two telopeptides at each end. The rest of the molecule experiences compression. When collagen tissue is stressed, it stretches for two reasons: (a) the waviness of the collagen fibers (which in their normal state have a slight bend every 100 μm of their length) decreases[22], and (b) the molecules elongate. Cowen *et al*[23] used electron microscopy data to show that most of the stretching is due to an increase in the D-period.

The distance between fibrils continues to diminish as the pore space between the ends of individual molecules diminishes. Consequently, the shrinkage rate increases almost tenfold in this third shrinkage rate period. This increase in shrinkage rate can be best appreciated if one considers that in the first two stages chrome cowhide loses 130% moisture while experiencing less than 2% shrinkage, whereas it shrinks an additional 8% while losing only 36% moisture in the third stage.

Figure 1 shows that Freudenberg[17] observed a decrease in shrinkage rate when the leather had a moisture content of 27%. Spiers and Pearson[18] found a decrease in percent shrinkage rate, i.e. percent shrinkage per unit weight of water lost, at about the same moisture content when the percent shrinkage in the third shrinkage step was 6.85%. With the length of the molecule plus the gap being 340 nm, a shrinkage of 6.85% is equal to 23.3 nm. To undergo this decrease in length, the gap had to shrink from 36 nm to 13 nm. It is interesting that Chandross and Bear[12] report a decrease of 22 nm in the gap zone (from 36 to 14 nm) at 18% moisture content. Closer examination of the above experimental data reveals that both papers report an average moisture content. There is, therefore, no reason to believe that at 27% moisture content a change in the mechanism

of water fixation occurs as alluded to by Freudenberg. The drop in shrinkage reported was simply due to the great decrease in the rate of moisture removal which, in turn, was a consequence of the drop in hydrostatic pressure in small capillaries at the surface of the leather sample. Due to the rapid drying the surface had reached the equilibrium moisture content and had stopped shrinking while the center was still fairly wet. With the surface opposing further shrinkage a reduction in shrinkage rate was observed.

At 38°C, a 27% moisture content in chrome leather is in equilibrium with air at 80% R.H. With $P/P_s = 0.8$, equations (1a) and (1b) permit calculation of the gap distance remaining filled with moisture. It is found to be equal to 9 nm.

Furthermore, purely mechanical calculations yield the same answer. The Young's modulus of elasticity, E, for collagen[23] is 1×10^8 N/m^2. When its extension, ε, is 6.85%, a collagen molecule experiences a stress of

$$\sigma = E\varepsilon = (1 \times 10^8)(0.0685)$$

$$= 6.85 \times 10^6 \text{ N/m}^2$$

But the force acting between two molecules due to capillary attraction can be calculated from the expression[24]

$$F = \frac{\tau A}{d}$$

where A = area of a collagen molecule
and d = distance between molecules

Consequently,

$$\sigma = \frac{F}{A} = \frac{\tau}{d} = \frac{0.072}{d} \text{ N/m}^2$$

$$\text{and } d = 0.072/\sigma = 0.072/6.85 \times 10^6$$

$$= 10.5 \times 10^{-9} \text{ m} = 10.5 \text{ nm}$$

As can be seen from electron micrographs of positively stained fibrils, this 9-11 nm distance which remains filled with water at 27% moisture content is adjacent to the location of the d-bands. This region has a large concentration of negatively charged, carboxyl groups, which in chrome leather are reacted with chrome complexes. Under physiological conditions this region is filled with non-collagenous materials such as dermatan sulfate[14] most of which are removed during liming and other processing steps of leather manufacture. Obviously, this deposition of chrome may be able to limit further shrinkage and ultimate cementing together of the molecules of collagen. This may well be one of the important functions of chrome in the conversion of hide into leather. However, without experimental proof it is not possible to ascertain that $2d = d_g - 13$, i.e. that equation (2c) applies as it does to untanned hide.

While capillary forces cause shrinkage during drying, they are also instrumental in keeping the fibrils apart. The analytical approach used here indicates that little physical

contact should occur between fibrils if the moisture content is about 13% and the distance between molecules greater than 2 nm (see Table 1). Since the length of a lysine side chain of a collagen molecule is almost 1 nm, at distances smaller than 2 nm, covalent and ionic bonds as well as hydrogen bonds and Van der Waals attractions between side chains of neighboring fibrils become feasible. A 13% hide moisture is in equilibrium with air at 38.7% relative humidity. Interestingly, the survey made by Buck[25] showed that the average relative humidity of the drying air in American tanneries is about 35%. It is a well established fact that drying to lower moisture content, especially with higher temperatures, yields firmer leather. Based on the results obtained in this paper, moisture contents below 13% should be avoided in any part of the hide to prevent formation of permanent crosslinks. This can be accomplished only if the humidity of the air in the falling-rate period is kept above about 39%. According to the equilbrium moisture isotherm[1] at 40°C, air at 14% humidity is in equilibrium with 9% moisture in the leather. Using equations (1a) and (1b), d is found to be equal to 1 nm under these conditions (see Table 1).

When leather is constrained during drying, stresses are induced as it shrinks. The change in free energy exerted in retaining its area is equal to the Young's modulus of elasticity, E, times the volume of the sample, $\pi R^2 z$, if one assumes that its shape is a disk of radius R and thickness z. If the radius were to decrease by dR, the free energy would decrease by $2\pi REzdR$. The tendency of the leather to lower its free energy by shrinkage would be counterbalanced by changes in the forces exerted by, e.g., toggles or by friction forces of pasting plates equal to $2\pi Rzd\sigma$. At equilibrium, $2\pi Rzd\sigma = 2\pi REzdR$.

Integration and cancellation of terms yields

$$\sigma - \sigma_0 = E (R_0 - R)$$

Assuming a totally constrained piece of leather which is initially not under stress, $\sigma_0 = 0$. From shrinkage considerations presented previously, $R_0 - R = \delta(\Delta X)$, where ΔX is a change in moisture content in the range where E is valid. For chrome leather $E = 28 \times 10^6$ N/m^2 (calculated from experimental data cited by Kanagy[26]. By ignoring the first two and the last shrinkage stage which yield relatively little change, and by recalling that $\delta \sim \delta 3 \sim 0.2$ for the third high-rate shrinkage stage which starts at X2 = .48 and ends at X3 = .27, one obtains

$$\begin{aligned}\sigma &= E\,\delta 3\,(X2 - X3)\\ &= 28 \times 10^6\,(0.2)\,(0.48 - 0.27)\\ &= 1.17 \times 10^6 \text{ N/m}^2\end{aligned}$$

This result is in full agreement with published data[27].

Note that stress relaxation was completely ignored in the above calculations. Examination of published data[18,27] indicates that stress relaxation stops at the end of the constant-rate drying period as soon as the surface of the leather has become dry. This is probably due to the thin layer of dry material at the surface becoming strong enough to resist stretching. As mentioned above, calculation of the capillary attraction forces induced during drying shows that they are too strong to permit an increase in distance between the ends of molecules. Since there are no covalent cross-links between fibrils, the limited increases in volume of leather accomplished during drying by restraining the leather is probably due to movement of fibrils in opposite directions.

Additional studies are needed before it will be possible to calculate accurately the condi-

tions which induce case-hardening or the onset of cracking of leather. The above calculations are presented only to show that the stresses induced are in conformity with the deformations caused by water removal and to demonstrate the potential of the research approach developed.

Conclusion

At equilibrium, there is a direct relationship between the moisture in the air and the distances between fibrils and molecules comprising the fibers. The calculations presented demonstrate that water removal involves considerable movement of collagen molecules relative to each other, thereby providing opportunities that did not exist in the fully wet condition for new contacts between amino acid residues as well as between amino acid residues and glycosaminoglycans which lead to crosslinking reactions especially at the higher temperatures used during drying[28]. Whereas the physical properties of leather are believed to depend on the degree to which the constituent fibrous parts of the leather have remained dissociated, the capillary attraction approach presented in this paper should be useful in the selection of suitable drying conditions which would avoid crosslinking reactions capable of impairing leather quality. Furthermore, the mathematical method shown in treating shrinkage and tensile stress data may be extended to studies to prevent drying conditions yielding permanent deformation, case-hardening, or other defects of leather.

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